UV-Visible Spectroscopy

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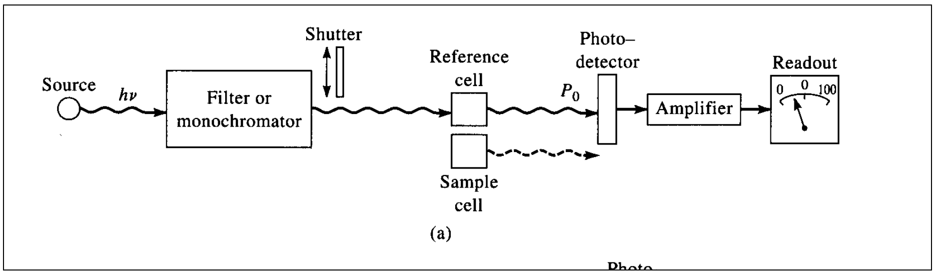
Components of instrumentation:

- Sources
- Sample Containers
- Monochromators
- Detectors

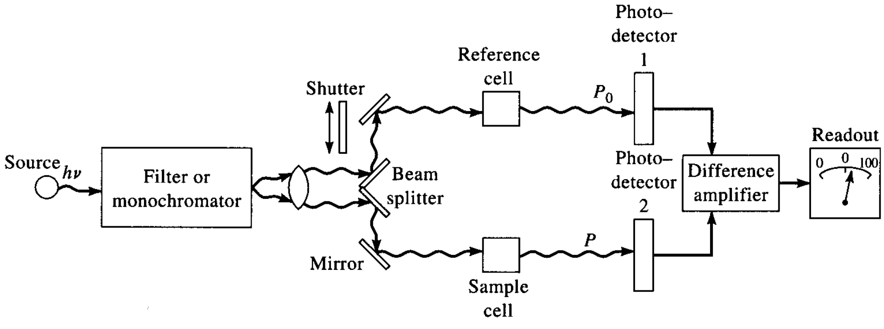
Components of instrumentation:

- Sources: Agron, Xenon, Deuteriun, or Tungsten lamps
- Sample Containers: Quartz, Borosilicate, Plastic
- Monochromators: Quarts prisms and all gratings
- Detectors: Pohotomultipliers

General Instrument Designs
Single beam



General Instrument Designs
Double Beam: Space resolved



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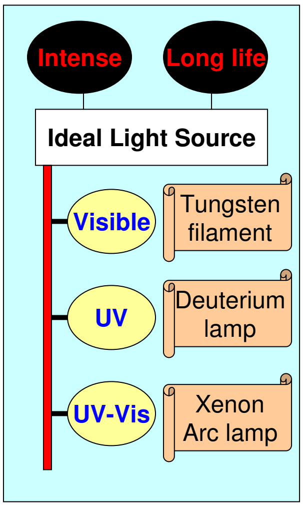
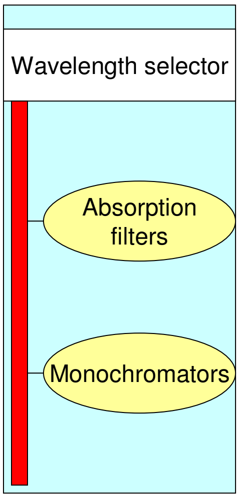
i. Sources

- An ideal light source used should:
  - Emits intense continuous spectrum of light across an entire region of the spectrum, such as the visible region.
- A light source used frequently for visible light absorption studies is the tungsten filament source and referred to as a colorimeter.
- A light source that can be used for both ultraviolet and visible studies is the xenon arc lamp and the instrument used is called UV-VIS spectrophotometer.
- Tungsten Filament Lamp
  - The tungsten filament is a source of visible light.
  - It is a light bulb with a tungsten filament and emits with visible wavelength with significant intensity.
  - However, the intensities of light varies dramatically across this wavelength range
- Deuterium Lamp
  - The deuterium lamp is a source of UV light.
  - It contains deuterium gas at a low pressure and emits UV light when electricity is applied across a pair of electrodes.
- Xenon Arc Lamp
  - The xenon arc lamp is a source for both visible and UV light.
  - It contains xenon at high pressure, and UV and visible are generated via a discharge across a pair of electrodes.



ii. Wavelength Selection

- Wavelength selection in a spectrochemical instrument actually consists of the selection of a narrow wavelength band from the larger band.
- The width of the band that is allowed to pass is called the bandwidth.
- The narrowness of the band that is allow to pass varies from one design to another is called the resolution.
- In order to plot the absorption spectrum of a molecule compound or complex ion:
  - We must be able to carefully control the wavelengths from the broad spectrum of wavelength emitted by the source.
  - So that we can measure the absorbance at each wavelength.
- In order to perform quantitative analysis by Beer's Law, we need to be able to carefully select the wavelength of maximum absorption, in order to plot the proper absorbance at each concentration.
- Thus we must be able to filter out the unwanted wavelengths and allow only the wavelength of interest to pass.



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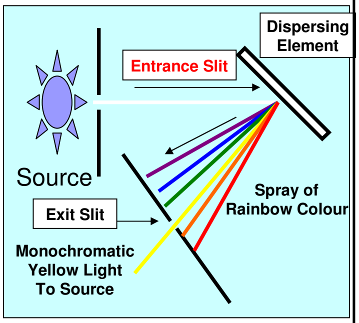
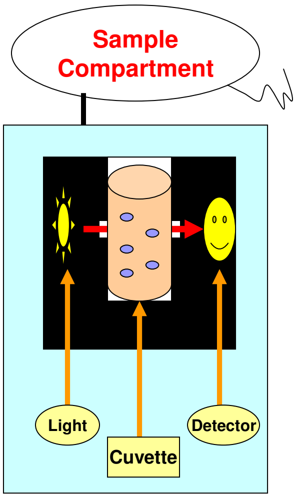
iii Monochromators

- A **slit** is a small circular or rectangular hole cut in an otherwise opaque plate, such as a black metal plate.
- The size of the opening is often variable – a variable **slit width**.
- The **entrance slit** is where light enters the monochromator from the source.
- Its purpose is to create a **unidirectional beam** of light of appropriate intensity from the **multidirectional light** emanating from the source.
- Its **slit width** is usually variable so that the intensity of the beam can be adjusted – the wider the opening the more intense the beam



iv. Sample Compartment

- Following the wavelength selection by the monochromator, the **beam** passes on to the **sample compartment** where the sample solution, held in **cuvette**, is positioned in its path.
- The **sample compartment** is an enclosure with a lid that can be opened and closed in order to insert and remove the cuvette.
- The **cuvette** is held tightly in a spring-loaded holder.
- Types of spectrophotometers:
  - **Single-beam** instruments
  - **Double-beam** instruments
- In a double-beam instrument the light beam emerging from the monochromator is split into two beams at some point between the monochromator and the detector.
- The double-beam design provides certain advantages that we will discuss shortly.



Single-Beam Spectrophotometer

- The **monochromatic light beam** created by the **monochromator** passes directly through the **sample solution** held in the **cuvette** and then proceeds to the **detector**.
- The most **inexpensive** design and is especially **useful** for routine absorbance measurements for which **wavelength of maximum absorbance** (the wavelength to be used) is **known in advance** without having to scan a particular wavelength range to determine it.
- **Advantages** of a **double-beam** instrument over a **single-beam** instrument:
  - Do not have **continually replace sample with blank** when obtaining a molecular absorption spectrum.
  - **Errors** due to **light source** and **detector fluctuations** are **minimized**.
  - Accurate **rapid scanning** of wavelengths is possible.

Double-Beam Spectrophotometer

- **Double-beam** means that the **light beam** produced by the **monochromator** is split into **two beams**.
- This is usually done in one of two ways:
  1. **Slotted mirror** – called a **beamsplitter**
  2. **Rotating circular partial mirror** – **light chopper**

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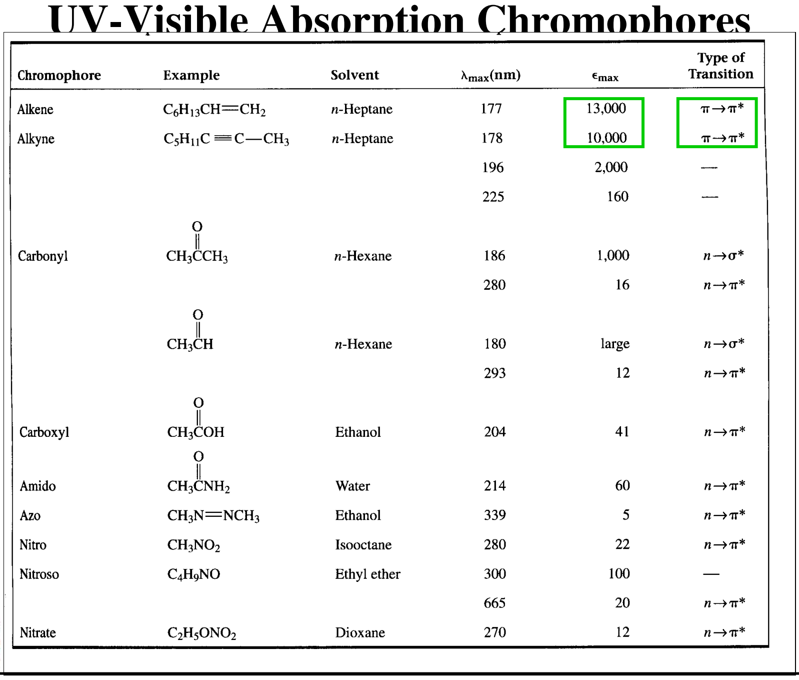
v. Detectors

- There are **TWO** types detectors used in UV-VIS spectrophotometers:
  - **Photo**multiplier tubes
  - **Photo**diodes
- While **thermocouples** (**heat sensors**) are used as detectors for infrared (IR) spectrometry.
- This is the reason **UV-VIS** instruments are called **spectrophotometers** while **IR** instrument are called **spectrometers**.

UV-Visible Absorption Chromophores



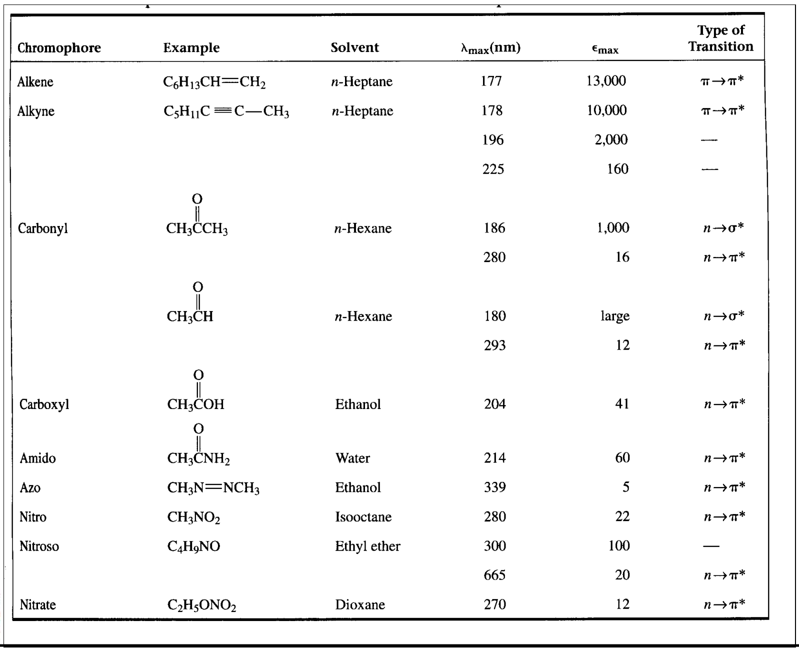
Chromophore	Example	Solvent	λ_{max}(nm)	ϵ_{max}	Type of Transition
Alkene	$C_6H_{13}CH{=}CH_2$	*n*-Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C{\equiv}C{-}CH_3$	*n*-Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2,000	—
			225	160	—
Carbonyl	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	*n*-Hexane	186	1,000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\overset{O}{\overset{\|}{C}}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	$CH_3\overset{O}{\overset{\|}{C}}OH$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\overset{O}{\overset{\|}{C}}NH_2$	Water	214	60	$n \rightarrow \pi^*$
Azo	$CH_3N{=}NCH_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Effects of solvents

- Blue shift (n- π*) (Hypsocromic shift)
  - ☐ Increasing polarity of solvent → better solvation of electron pairs (n level has lower E)
  - ☐ → peak shifts to the blue (more energetic)
  - ☐ 30 nm (hydrogen bond energy)

- Red shift (n- π* and π –π*) (Bathochromic shift)
  - ☐ Increasing polarity of solvent, then increase the attractive polarization forces between solvent and absorber, thus decreases the energy of the unexcited and **excited states** with the later greater
  - ☐ → peaks shift to the red
  - ☐ 5 nm

UV-Visible Absorption Chromophores



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Effects of Multiple Chromophores

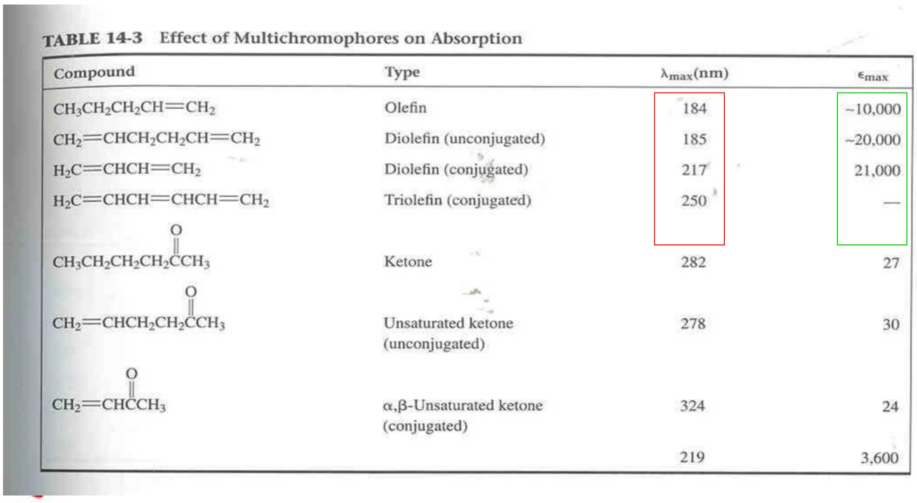

TABLE 14-3 Effect of Multichromophores on Absorption

Compound	Type	λ_{max}(nm)	ϵ_{max}
$CH_3CH_2CH_2CH{=}CH_2$	Olefin	184	~10,000
$CH_2{=}CHCH_2CH_2CH{=}CH_2$	Diolefin (unconjugated)	185	~20,000
$H_2C{=}CHCH{=}CH_2$	Diolefin (conjugated)	217	21,000
$H_2C{=}CHCH{=}CHCH{=}CH_2$	Triolefin (conjugated)	250	—
$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	Ketone	282	27
$CH_2{=}CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	Unsaturated ketone (unconjugated)	278	30
$CH_2{=}CH\overset{O}{\overset{\|}{C}}CH_3$	α,β-Unsaturated ketone (conjugated)	324	24
		219	3,600

Now solvents are your "container"

- They need to be transparent and do not erase the fine structure arising from the vibrational effects

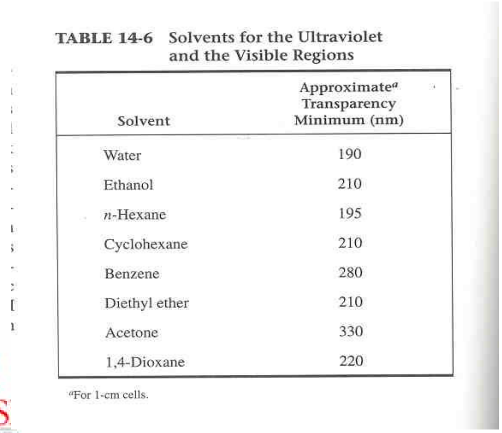

TABLE 14-6 Solvents for the Ultraviolet and the Visible Regions

Solvent	Approximate[a] Transparency Minimum (nm)
Water	190
Ethanol	210
n-Hexane	195
Cyclohexane	210
Benzene	280
Diethyl ether	210
Acetone	330
1,4-Dioxane	220

[a]For 1-cm cells.

Polar solvents generally tend to cause this problem

Same solvent must be Used when comparing absorption spectra for identification purpose.

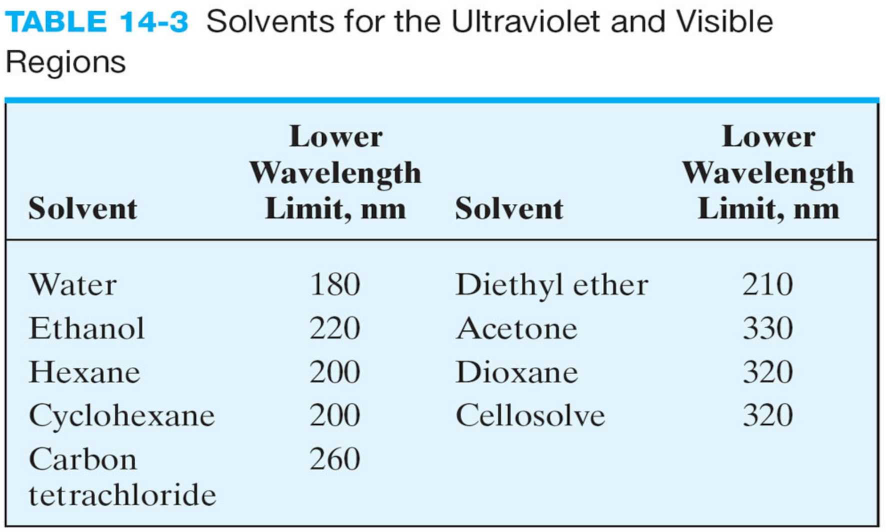

TABLE 14-3 Solvents for the Ultraviolet and Visible Regions

Solvent	Lower Wavelength Limit, nm	Solvent	Lower Wavelength Limit, nm
Water	180	Diethyl ether	210
Ethanol	220	Acetone	330
Hexane	200	Dioxane	320
Cyclohexane	200	Cellosolve	320
Carbon tetrachloride	260		

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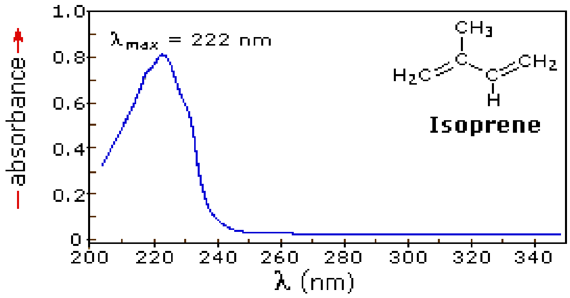
List of common chromophores and their transitions

TABLE 9.1 Summary of UV λ_{max} and Transition Types for Simple Chromophores

Chromophore	*Compound*	*Transition*	λ_{max} (nm)	ε
C–H	CH_4	$\sigma\rightarrow\sigma^*$	122	
C–C	C_2H_6	$\sigma\rightarrow\sigma^*$	135	
C=C	C_2H_4	$\pi\rightarrow\pi^*$	103	15000
			174	5500
C=C=C	C_3H_4	$\pi\rightarrow\pi^*$	170	4000
			227	630
C≡C	R–C≡C–R´	$\pi\rightarrow\pi^*$	178	10000
			196	2000
			223	160
C–O	R–O–R	$n\rightarrow\sigma^*$	180	500
C–O	R–O–R´	$n\rightarrow\sigma^*$	180	3000
C–N	Amino	$n\rightarrow\sigma^*$	190-200	2500-4000
C–S	R–S–H	$n\rightarrow\sigma^*$	195	1800
C–S	R–S–R	$n\rightarrow\sigma^*$	235	180
C=O	Aldehyde/Ketone	$n\rightarrow\sigma^*$	166	16000
		$\pi\rightarrow\pi^*$	189	900
		$n\rightarrow\pi^*$	270	10-20
C=O	Carboxylic acid	$n\rightarrow\pi^*$	200	50
C=O	Carboxylate	$n\rightarrow\pi^*$	210	150
C=O	Ester	$n\rightarrow\pi^*$	210	50
C=O	Amide	$n\rightarrow\pi^*$	205	200
C=N	$(NH_2)_2C{=}NH$	$n\rightarrow\pi^*$	265	15
C≡N	$CH_3C{\equiv}N$	$\pi\rightarrow\pi^*$	<170	
N=N	Me–N=N–Me	$n\rightarrow\pi^*$	350-370	15
N=O	Me_3NO	$n\rightarrow\pi^*$	300	100
			665	120
N=O	Me_3NO_2	$n\rightarrow\pi^*$	276	27
C=C=O	$Et_2C{=}C{=}O$	$\pi\rightarrow\pi^*$	227	360
		$n\rightarrow\pi^*$	375	20
C–Cl		$n\rightarrow\sigma^*$	173	200
C–Br		$n\rightarrow\sigma^*$	208	300
C–I		$n\rightarrow\sigma^*$	259	400

Organic Compounds



- Most organic s
- Electronic and
- Absorption bands usually broad
- Detailed theoretical analysis not possible, but semi-quantitative or qualitative analysis of types of bonds is possible.
- Effects of solvent & molecular details complicate comparison

Rule of thumb for conjugation

If greater then one single bond apart
- ε are relatively additive (hyperchromic shift)
- λ constant

$CH_3CH_2CH_2CH=CH_2$	λ_{max}= 184	ε_{max} = ~10,000
$CH_2=CHCH_2CH_2CH=CH_2$	λ_{max}=185	ε_{max} = ~20,000

If conjugated
- shifts to higher λ's (red shift)

$H_2C=CHCH=CH_2$	λ_{max}=217	ε_{max} = ~21,000